

Short Communication

LEWIS ACIDITY AND COKING OF HYDRODESULFURIZATION CATALYSTS

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INTRODUCTION

For hydrodesulfurization of residual oils it has been reported that proprietary coke-resistant catalysts possess, in the oxidic state, a low level of Lewis acidity [1]. This suggests that Lewis acid sites on catalyst surfaces may participate in coke-forming reactions. While there is general consensus that coking reactions over HDS catalysts are indeed acid catalyzed, there is, however, disagreement as to the relative importance of Brönsted and Lewis acidities on the catalysts. This note presents evidence of the active participation of Lewis acid sites in the reactions that lead to coke formation on HDS catalysts.

EXPERIMENTAL

Laboratory coking experiments were performed over a HDS catalyst using anthracene, phenanthrene and 9,10-dihydroanthracene. Although the detailed chemistry of coke formation from these compounds is only partially understood, it is known that anthracene will undergo Lewis-acid-catalyzed dehydrogenation—condensation reactions [2]. The evidence, including ESR and ¹H-NMR data, indicates that the initial reactions proceed via a radical cation mechanism. Major reaction products of anthracene dehydrogenation—condensation reactions are higher oligomers of anthracene. Once a certain level of dehydrogenation, condensation and molecular weight increase has been achieved, the reaction product can be classified as “coke”. Commonly, coke is defined quantitatively as material insoluble in pyridine and/or quinoline. This study is an attempt to establish, if possible, a correlation between the ability of various HDS catalysts to catalyze the coking of anthracene and their Lewis acidities.

The principal catalyst used was a proprietary HDS catalyst (3 wt% Co

and 10 wt% Mo on γ -Al₂O₃). In addition, γ -Al₂O₃ loaded to levels of 0, 3, 8 and 12 wt% Mo as MoO₃ was tested. The HDS catalyst was prepared in both the oxidic and sulfided state. The sulfiding conditions were those which have been reported to give maximum hydrodesulfurization of benzothiophene [3]; they are, heat treatment in air for 3 h at 523 K, followed by sulfidation for 1 h at 523 K and 1 atm of a flowing mixture of 6 vol% H₂S in H₂. The level of sulfur uptake corresponded to that required for almost complete conversion of Mo to MoS₂ and Co to Co₉S₈ [4].

Tested also was the effect of the addition of pyridine, a strong Lewis base, to the catalyst and anthracene/catalyst mixtures for the HDS catalyst and the 12 wt% Mo-Al₂O₃ catalyst. Pyridine addition corresponded to 0.20 mmol/g for the HDS catalyst and 0.21 mmol/g for the 12 wt% Mo-Al₂O₃ catalyst. These were the amounts of pyridine retained by the catalysts following pyridine vapor adsorption and desorption isotherms. The adsorptions were conducted at 298 K to a relative vapor pressure of 0.96 and the initial desorptions were at 10 Pa and 298 K for 24 h followed by further desorptions at 383 K for 24 h. These times were sufficient to reach constant weight.

The coking experiments were performed in batch tubing reactors similar to those described previously [5]. The 15 cm³ reactors were charged with 1 g anthracene and 3 g catalyst, evacuated to 30 Pa, flushed with N₂, then pressurized to 6.9 MPa of N₂. Reactions were performed isothermally in a fluidized-bed sandbath. Heating to reaction temperature was achieved in less than 3 min. Subsequent to reaction, quenching in a waterbath to 298 K was achieved in less than 1 min. Conversion of the organic compound to coke was determined by Soxhlet extraction with boiling pyridine for 24 h under N₂. Residual pyridine was removed by evacuation (383 K, 10 Pa, 48 h).

RESULTS AND DISCUSSION

Conversion data are given in Table 1 for various catalyst conditions. The data represent the conversion of anthracene into pyridine-insoluble material for reaction at 668 K for 30 min. Comparison is made on the basis of equal weight for each catalyst. This is valid since surface areas (N₂ at 77 K) varied only from 140 m²/g for the γ -Al₂O₃ to 130 m²/g for the HDS catalyst loaded with metals. In the absence of added catalyst and in the presence of γ -Al₂O₃, no significant conversion of anthracene to coke was observed for these reaction conditions. In the absence of added catalysts, anthracene coking is thought to proceed via a series of free radical polymerization—condensation reactions [6]. However, the rate is considerably slower than in the acid-catalyzed case, which is associated with a radical cation mechanism. As will be reported elsewhere, γ -Al₂O₃ displays almost no catalytic activity towards the coking of anthracene over a wide range of coking conditions.

The conversion of anthracene to coke increased linearly (Fig. 1) with increasing MoO_3 loading on the $\gamma\text{-Al}_2\text{O}_3$. This can be correlated with data presented previously showing an increase in total acidity of HDS catalysts [7] and an increase in their capacity to form cations from anthracene

TABLE 1

Conversion of anthracene to coke over various catalysts

Reaction conditions: 1 g anthracene, 3 g catalyst, 668 K, ^{0.5 h} 0,05 h, 6.9 MPa N₂

Catalyst	Catalyst condition	Anthracene conversion to pyridine insolubles (wt%)
None	—	0
$\gamma\text{-Al}_2\text{O}_3$	oxidic	0
3 wt% Mo— Al_2O_3	oxidic	15.8
8 wt% Mo— Al_2O_3	oxidic	33.4
12 wt% Mo— Al_2O_3	oxidic	47.6
	oxidic, pyridine added	11.8
3 wt% Co, 10 wt% Mo— Al_2O_3	oxidic	38.6
	sulfided	39.7
	oxidic, pyridine added	9.5
	oxidic, acridine added	9.0

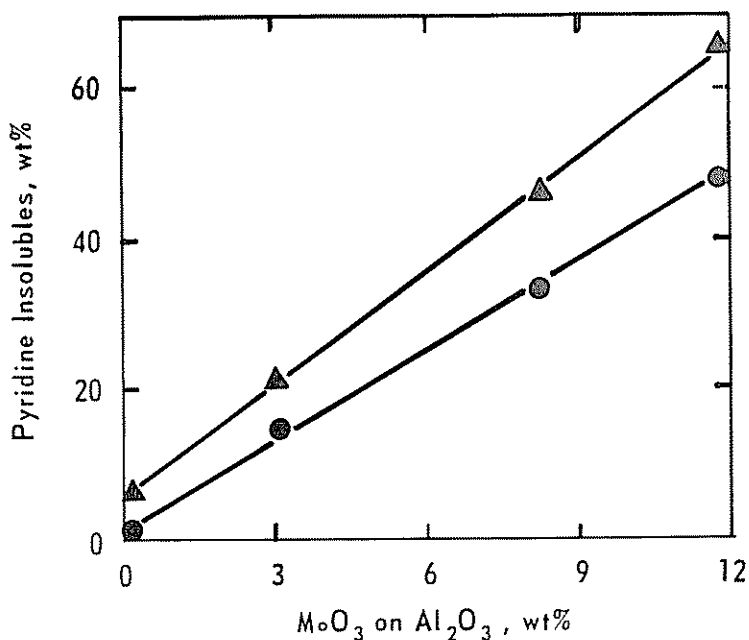


Fig. 1. Effect of MoO_3 loading on $\gamma\text{-Al}_2\text{O}_3$ on the coking of anthracene; \circ , 30 min at 668 K; \triangle , 698 K.

[8] as the MoO_3 loading on Al_2O_3 is increased. This corresponds also to an increasing ability of the catalyst to retain absorbed pyridine, which may be a measure of the strength of surface Lewis acidity. Pyridine retention data are given in Fig. 2 for various MoO_3 loadings.

The implication of the data in Figs. 1 and 2 is that the same surface sites may be associated with the coking of anthracene and the adsorption of pyridine. This was confirmed, to some extent, by coking anthracene over the HDS catalyst on which pyridine had been pre-adsorbed to an uptake of 1.6 wt%. The data of Fig. 3 indicate that the presence of pyridine resulted in a diminished yield of coke from anthracene. Apparently, adsorption of pyridine on to the Lewis acid sites on the HDS catalyst blocks their participation in the coking reactions of anthracene. The pyridine-adsorbed HDS catalyst did maintain a coking activity in excess of that for the Al_2O_3 support. This may indicate that not all the Lewis acid sites were occupied

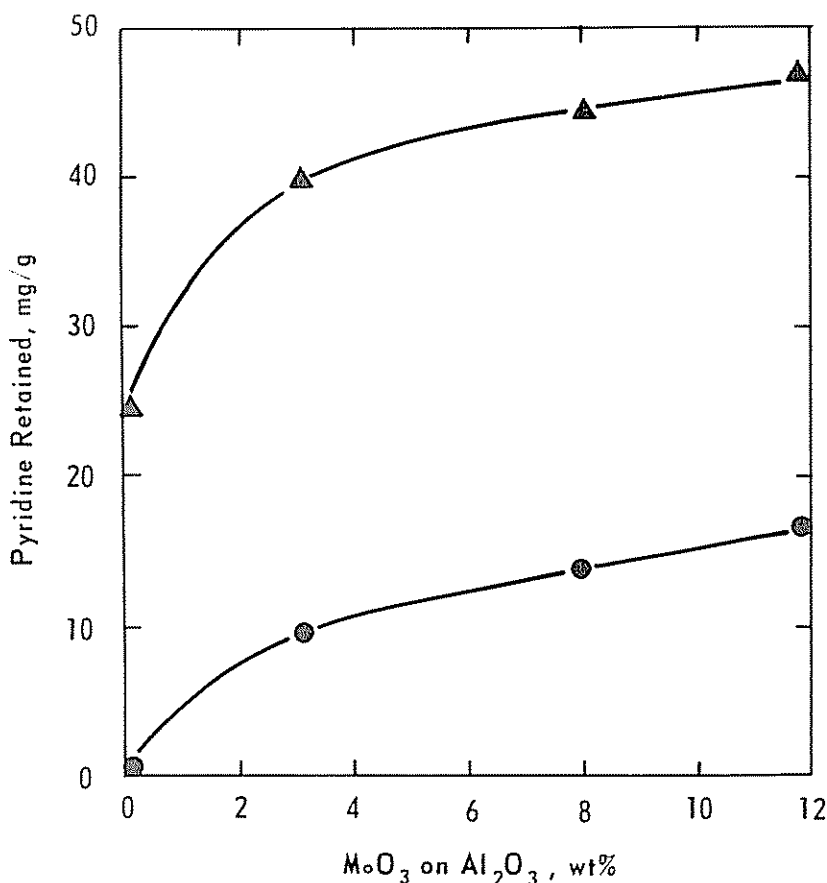


Fig. 2. Effect of MoO_3 loading on $\gamma\text{-Al}_2\text{O}_3$ on the retention of pyridine after evacuation for 24 h; ▲, 10 Pa at 298 K; ●, 383 K.

by pyridine molecules at the reaction conditions. Some pyridine desorption is expected to occur at the high reaction temperature. It is noted that acridine also effectively reduced coke formation on the HDS catalyst (Table 1).

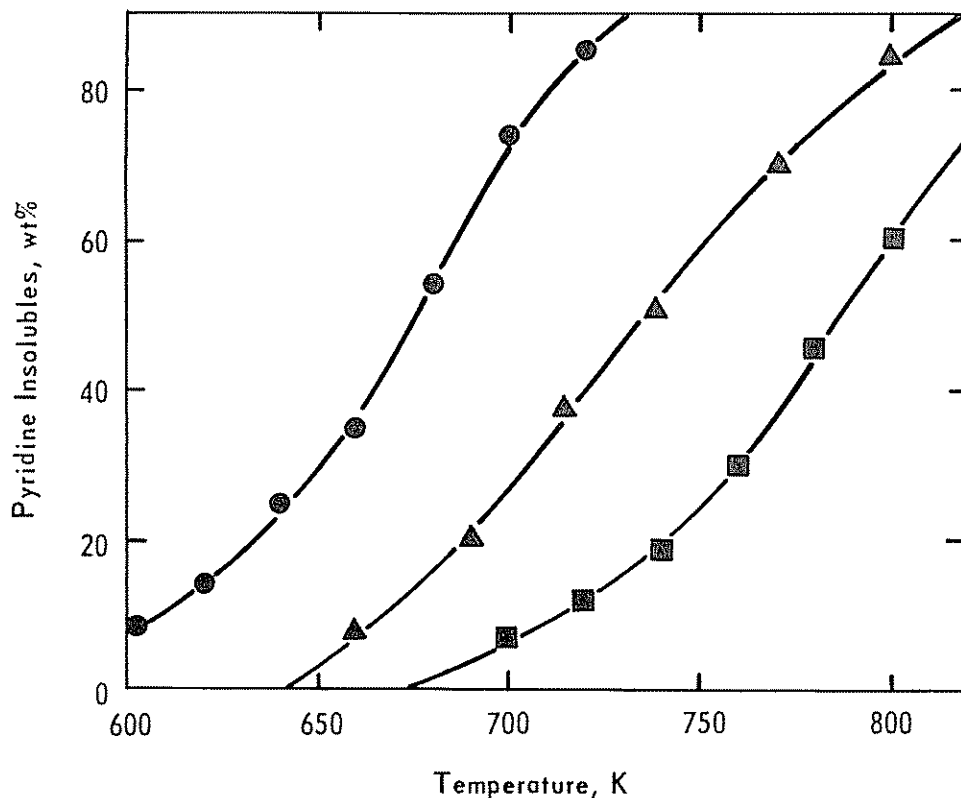


Fig. 3. Effect of adsorbed pyridine on the coking of anthracene over the Co-Mo-Al₂O₃ catalyst and support for 60 min; ■, Al₂O₃; ●, Co-Mo-Al₂O₃; ▲, pyridine + Co-Mo-Al₂O₃.

For the HDS catalyst, the level of conversion did not depend on whether the catalyst was initially in the oxidic or sulfided state (see Table 1). This is significant since it has been inferred from the IR spectrum of adsorbed pyridine that Brønsted acid sites on Co-Mo-Al₂O₃ catalysts disappear upon sulfiding [9] but that Lewis acidity remains. This is consistent with the retention of catalytic coking activity in the sulfided state based on a mechanism involving Lewis acid sites. Furthermore, hydrogen gas is a major product of the dehydrogenation-condensation reactions of anthracene. At 668 K in a reducing atmosphere, it has been shown that Brønsted acidity is lost rapidly, whereas Lewis acidity increases with time [10].

Therefore, Brönsted acidity in the initially oxidic catalyst would be rapidly lost, preventing its participation in the coking process.

Both phenanthrene [11] and 9,10-dihydroanthracene [12] are known also to undergo Lewis-acid-catalyzed dehydrogenation—condensation reactions but at much slower rates than anthracene. The conversion to pyridine insolubles over the HDS catalyst at 668 K for 1 h was: anthracene (47.2%) > 9,10-dihydroanthracene (14.7%) > phenanthrene (1.7%). This is further evidence of a major role of Lewis acid sites in the coking of hydrosulfurization catalysts. The high reactivity of 9,10-dihydroanthracene relative to phenanthrene is not consistent with base strengths and implies different mechanisms. Possibly, 9,10-dihydroanthracene is converted to anthracene via H₂ elimination. The anthracene may then undergo Lewis-acid-catalyzed condensations or may react with cations produced from 9,10-dihydroanthrene.

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